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BORATION OF COBALT AND ALLOYS BASED ON COBALT

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Pages 30-41

Only a few studies (Ref. 1, 2) have been devoted to the boration of cobalt.

Attention has been given to a study of borating cobalt and alloys based upon it due to the fact that one of the cobalt alloys (K40NKhM) is used for the manufacture of nonmagnetic, corrosionary stable springs and core samples of electrical measuring instruments. In addition, the hardness of core samples from this alloy, which equals HRC 58-61, is insufficient for certain instruments. Therefore it is of practical interest to study the possibilities of increasing the hardness of this alloy by means of boration.

BORATION OF COBALT

Boration was done by electrolysis in a melted drill and in a melted draw with the introduction of boron carbides (up to 30-40% by weight). The latter boration method is described in Work (3). p. 16

Boration by drill electrolysis was done at a temperature of 950°C. It can be seen from figure 1 that with an increase in the density current, depth and surface hardness of the layer sharply increased at first, and then decreased with a further increase in the current density. Apparently, at first the formation of atomic boron on the cathode is accelerated with an increase in the current density. With a further increase in the current density, there apparently occurs either intensive dissolution of the sample surface in the melt (this is observed during certain diffusion processes carried out during electrolysis of salts), or a deposit is formed on the sample surface, preventing absorption of the atomic boron metal by the surface.

When a bath which could operate for a long period of time was used, an anomaly was also found in the change of the

microstructure, the surface hardness, and the layer depth depending upon the duration of the process. If the determined length of the process was exceeded (6-15hrs), the surface microhardness sharply fell, reaching the hardness of unborated cobalt.

This was accompanied by a change in the microstructure and by a decrease in the overall depth of the borated layer. A faintly etched border of significant thickness having a lower microhardness than the microhardness of cobalt (Figure 2) appeared on the microstructure of the surface zone of the borated layer. Spectral analysis showed that this deposit consisted primarily of nickel, iron, and chromium, which could enter into the draw melt from the Michrome crucible and the Michrome wire, on which samples were suspended. Obviously a decrease in the borated layer depth with large current densities can also be explained by the precipitation of an amalgous deposit on the surface samples.

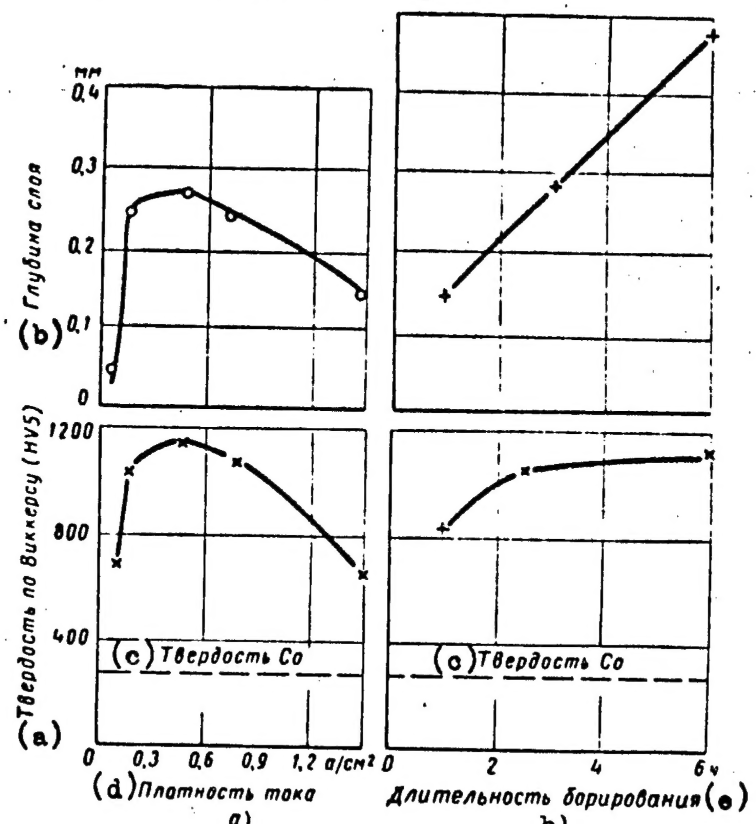


Fig 1. Effect of the current density and the duration of electrolytic boration at a temperature of 950°C on the depth and hardness of the borated cobalt layer (the distance from the surface to the end of the longest needles was used as the layer depth).
a). Hardness according to Vickers (HV5);
b). Layer depth; c). Co hardness; d). Current density; e). Duration of boration.

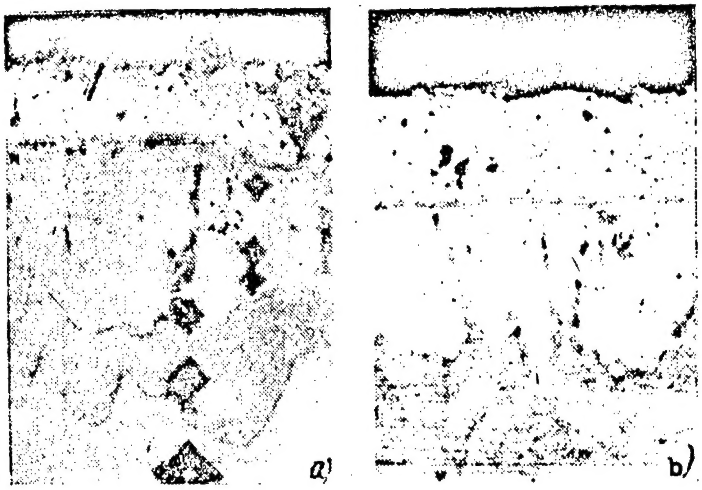


Fig 2. Microstructure of the cobalt surface layer after electrolytic boration at a temperature of 950°C (current density 1.5a/cm^2). Treatment was carried out in a long-operating bath for 6 hours (a) 12 hours (b). X200

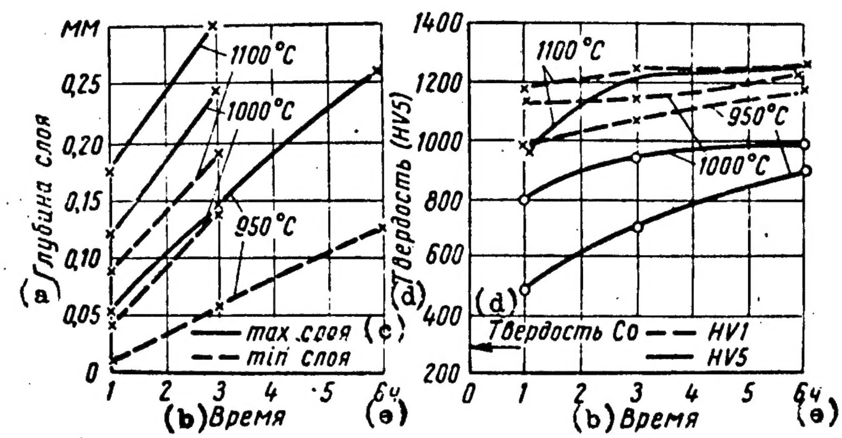


Fig 3. Effect of temperature and duration of boration in a melted drill with boron carbide upon the depth and hardness of the borated cobalt layer (the distance from the surface to the end of the longest needle is used as the maximum layer depth, and the minimum is - the thickness of the solid boride layer.
a) layer depth; b) time ; c) layer; d) Hardness; e) hours.

A comparison of electrolytic cobalt boration (see Fig 1.) with boration in a melted draw with boron carbide (Fig 3 and 4) shows that the formation of the borated layer takes place approximately two times slower than the second method, but the state of the sample surfaces obtained is always very good (after washing in hot water, the surface is absolutely pure and slightly dull). Furthermore, with boration by the second method the necessity of close contact between the current conducting wire and the samples is eliminated.

It can be seen from Fig 4 that in the boration of cobalt two borides are formed with different microhardness - about H_{100} 1550 and 1800. With electrolytic boration, both borides are formed after 3 hrs, while with the second boration method both borides are formed only after 6 hrs.

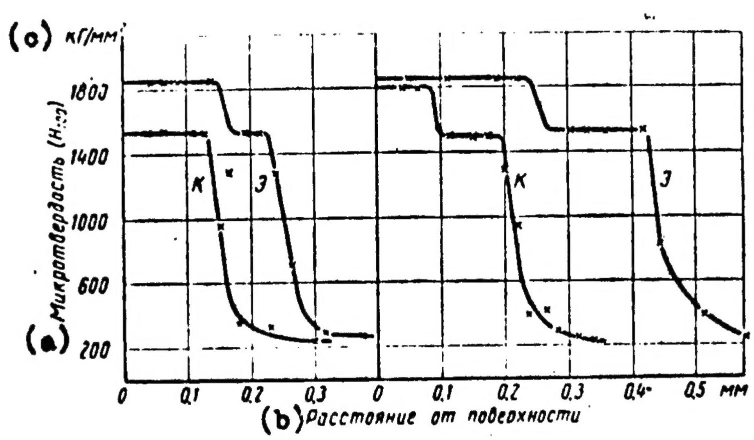


Fig 4. Distribution of microhardness by depth of borated cobalt layer (950°C for 3 hrs - curves on the left, and for 6 hrs - curves on the right): Э - electrolytic boration; K - boration in a melted draw with boron carbide. a) microhardness (H_{100}); b) distance from the surface.; c) kg/mm^2

The microstructure of the borated cobalt layer is similar to the microstructure of the borated layer of steel and at a small layer depth it resembles a weakly etched zone wedged in the cores in the form of needles (Fig 5, a). If the length of the process is increased, during boration on microstructures a second phase is clearly revealed in the surface zone of the layer, the needles of which are wedged into the first phase (Fig 5, b).

X-ray diffraction analysis (Table 1) revealed the presence in the layer of two borides: Co_2B and CoB (according to the diagram for the composition of Co-b, the first boride contained 8.41%B and the second - 15.51%B)(Ref 4). Ananalysis also showed that the second harder boride CoB, which was richer in boron is formed in the surface zone of the layer only after more than 3 - 6 hrs, which completely agrees with data obtained previously from microanalysis and from the distribution of microhardness according to the layer depth.

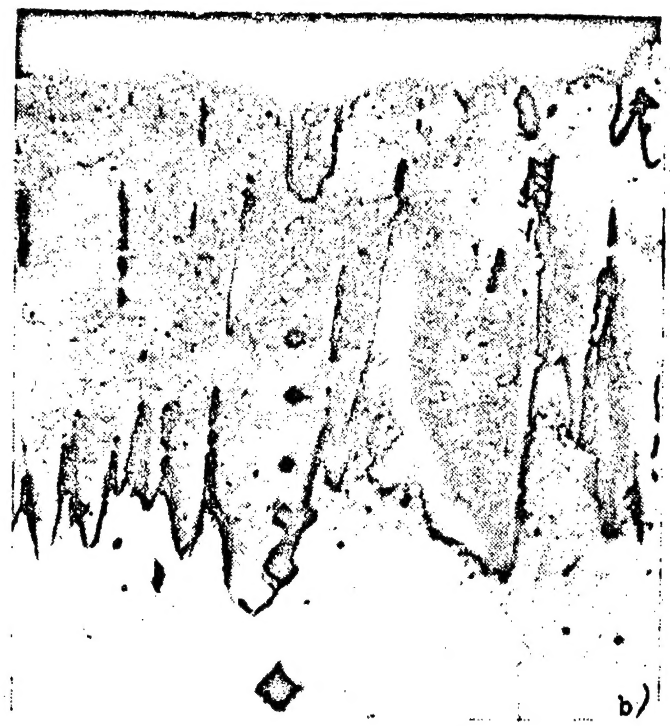


Fig 5. Microstructure of cobalt subjected to electrolytic boration at a temperature of 950°C for 3 hrs (a) and for 6 hrs (b). X200.

Table 1.

Results of X-ray diffraction analysis of borated cobalt (boration temperature of 950°C for 6 hrs)

(a) Место съемки рентгенограммы	(b) Эксперимен-тальные данные: параметры решетки	(c) Литературные данные [4]		
		(d) Параметры решетки	(e) Тип решетки	(f) Борид
(g) Поверхность образца	$a = 4{,}050$	$a = 3{,}956$	(h) Ромбическая	CoB
	$b = 5{,}295$	$b = 5{,}253$		
	$c = 2{,}946$	$c = 3{,}043$		
Слой на глубине 0,07 *мм* от поверхности (i)	$a = 5{,}054$	$a = 5{,}005$	(j) Тетрагональная	Co_2B
	$c = 4{,}219$	$c = 4{,}212$		

a) area photographed in the X-ray photograph; b) experimental data: Lattice parameters; c) source material (Ref 4) d) lattice parameters; e) type of lattice ; f) boride; g) sample surface; h) rhombic; i) layer at a depth of 0.07mm from the surface; j) tetragonal.

In a study of microstructures it was established that, at the boundary between boride Co_2B and the core, in a number of cases a conspicuous thin layer of an intermediate new phase is visible. Since the thickness of the zone at this phase is very small, it was not possible to measure its microhardness or to carry out X-ray diffraction analysis. Obviously this thin layer is boride Co_3B.

Fig 6 schematically shows the change in phase composition depending on the depth of the borated cobalt layer, content of boron, microhardness, and microthermoelectromotive force. Curves for the microthermoelectromotive force (Ref 5) completely reproduce the change in phase composition depending upon the depth of the borated layer (it was not possible to measure the microthermoelectromotive force of the very thin zone assumed to be related to Co_3B).

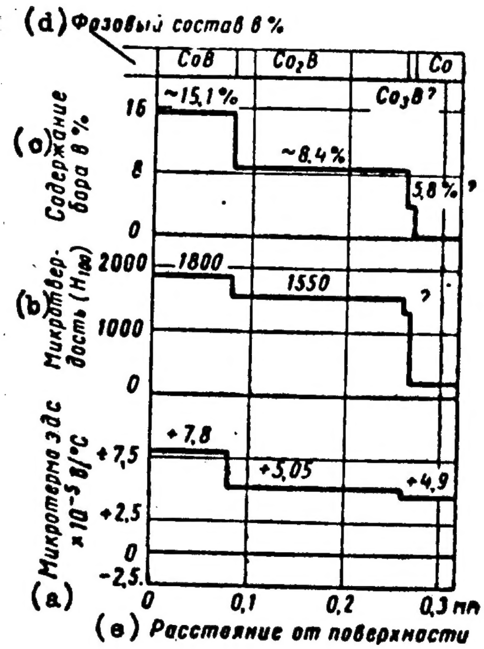


Fig 6. Change in phase composition, boron content, microhardness and microthermoelectromotive force depending on the depth of the borated cobalt layer (the microthermoelectromotive force was measured by engineer V. Ustogal in consultation with E. V. Panchenko). a) microthermoelectromotive force; b) microhardness; c) boron content in percent; d) phase composition in percent; e) distance from surface.

BORATION OF ALLOYS

The boration of alloys (Table 2) was carried out in a bath, consisting of a melted draw and boron carbide (30-40% by weight).

The dependence of the depth and the surface hardness according to Vickers of the borated alloy layers upon the duration and temperature of the process is shown in Fig 7.

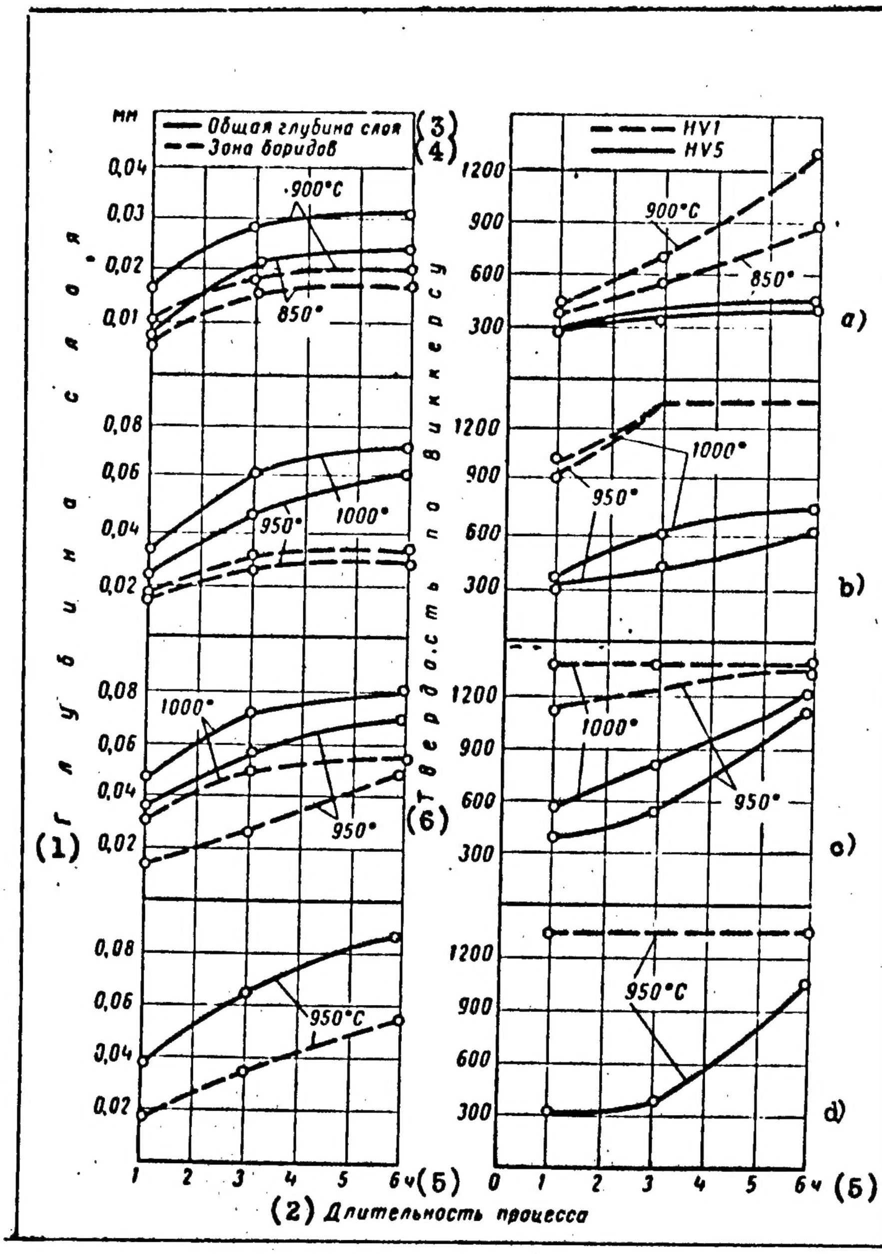


Fig. 7. Change in the depth and surface hardness of the borated alloy layers K40KhNM (a, b), K40Kh20 (c) and 36NKhTYu (d) depending on the duration of the boration at different temperatures. -- 1) Layer depth; 2) Duration of process; 3) General layer depth; 4) Boride zone; 5) Hours; 6) Vickers hardness.

Table 2
The chemical composition of
alloys subjected to boration

(a) Марка сплава	(b) Химический состав в %									
	C	Co	Cr	Ni	Mo	Al	Ti	Si	Mn	Fe
(e) K40НХМ	0,08—0,12	36—41	18—20	15—17	6—7	—	—	<0,5	0,8—1,2	Остальное (c)
(f) K40X20	—	До 40	До 20	—	—	—	—	<0,2	<0,2	То же (d)
(g) 36НХТЮ	—	—	13	36	—	1	3	—	—	»

a) type of alloy; b) chemical composition in percent; c) remainder; d) the same; e) K40NKhM; f) K40Kh20; g) 36NKhTYu.

The boration of the alloys K40Kh20 and 36NKhTYu takes place somewhat faster than does the alloy K40KhNM. The surface microhardness of all the alloys is approximately the same and amounts to about H_{100} 2300, i.e., greater than the microhardness of the surface layer of the borated cobalt.

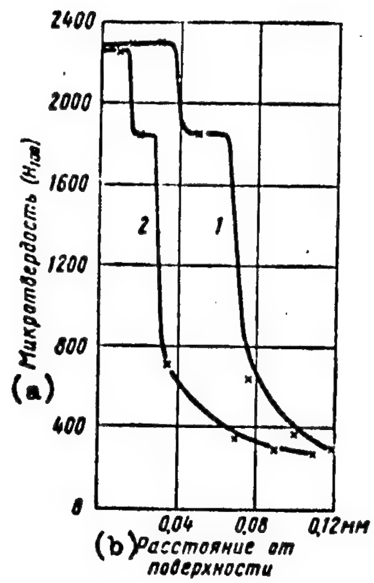


Fig 8. Distribution of the microhardness on the surface layer of the alloys borated at a temperature of 1,000°C for 6 hrs: 1 - the alloy K40Kh20; 2 - the alloy K40KhNM. a) microhardness (H_{100}); b) distance from the surface.

The diffusion layer in the alloys consists of several zones (Table 3). The surface zone which is only slightly etched is the zone of borides. The outer part of this zone is etched somewhat more strongly (the lower series of microstructures) and - according to data derived from X-ray diffraction analysis of the alloys K40KhNM and K40Kh20, carried out under the guidance of L. N. Rastorguev - presents a rhombic boride of the type CoB and FeB. The inner part of this zone which is just barely etched, represents a tetragonal boride of the type Co_2B and Fe_2B (Table 4).

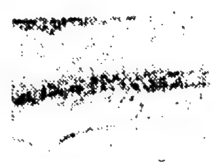
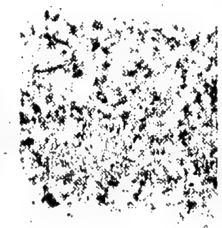
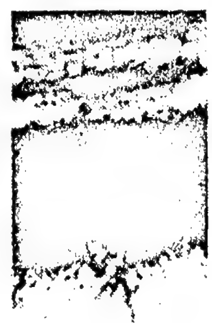
X-ray diffraction analysis did not indicate the presence of three borides of chromium, nickel and molybdenum in the layer; apparently part of the cobalt and iron atoms in the crystal lattice of the borides were replaced by chromium nickel and molybdenum.

The microhardness of borides of the type (Co, Fe, Cr, Ni, Mo)B; (Co, Fe, Cr)B, located on the surface itself, was practically the same for both of the alloys studied (Fig 8) and amounted to about H_{100} 2300. This is related to the borides located at deeper depths of the type $(Co, Fe, Cr, Ni, Mo)_2B$ and $(Co, Fe, Cr)_2B$, the hardness of which in both alloys amounts to about H_{100} 1850.

The transition zone of the layer has a low hardness which is clearly etched (especially in the alloy K40KhNM) and has a different microstructure in the various alloys.

Table 3

Microstructure of borated alloy layers. X600

(a)	(b)	(c)		
К40ХНМ (d)	1 000			
К40ХНМ (d)	950			
К40Х20 (e)	1 000			

a) the alloy to be borated; b) boration temperature in degrees C; c) boration time in hours ; d) K40KhNM; e) K40Kh20.

Table 4

Results of X-ray analysis of the borated alloys (temperature of 1,000°C, for 6 hrs)

(a) Марка сплава	(b) Место съемки рентгенограммы	(c) Тип решетки	(d) Параметры решетки	(a) Марка сплава	(b) Место съемки рентгенограммы	(c) Тип решетки	(d) Параметры решетки
К40ХНМ (i)	(e) Поверхность образца	(f) Ромбическая	$a = 3{,}985$ $b = 5{,}260$ $c = 3{,}070$	К40Х20 (j)	(e) Поверхность образца	(f) Ромбическая	$a = 3{,}920$ $b = 5{,}215$ $c = 2{,}970$
	(g) Зона слоя на глубине 0,02 *мм*	(h) Тетрагональная	$a = 5{,}020$ $c = 4{,}260$		(g) Зона слоя на глубине 0,02 *мм*	(h) Тетрагональная	$a = 5{,}06$ $c = 4{,}24$

a) type of alloy; b) area to be photographed in the X-ray photograph; c) type of lattice; d) lattice parameters; e) surface of the sample; f) rhombic; g) zone of the layer at a depth of 0.02mm; h) tetragonal ; i) K40KhNM; j) K40Kh20.

The microstructure and the depth of the borated layer in the alloy samples and in cobalt differ sharply from each other. The components of the alloys greatly retard the diffusion of boron. In connection with this, the diffusion of boron is intensified at the boundaries of the grain. This is clearly evident in microstructures (Table 3), where the boundaries of the grains located deeper than the transition zone are clearly etched.

We investigated other properties of boride layers which had great practical value - magnetic susceptibility, durability, and corrosional stability.

Table 5

The effect of the duration of boration at a temperature of 1,000°C upon the magnetic susceptibility of the alloys K40KhNM and K40Kh20.

(a) Марка сплава	(b) Длительность борирования в ч	(c) Масса в г	(d) Ток в а	(e) Магнитная восприимчивость в гс/э	(a) Марка сплава	(b) Длительность борирования в ч	(c) Масса в г	(d) Ток в а	(e) Магнитная восприимчивость в гс/э
(f) K40XHM	0	2,2601	0,11	1,0	(g) K40X20	0	4,2433	0,386	1,873
	1	1,9975	0,259	2,66		1	3,4748	0,52	3,08
	3	1,9649	0,34	3,55		3	3,4370	0,686	4,12
	6	2,1311	0,44	4,25		6	3,6211	1,01	5,70

a) type of alloy; b) length of boration in hours; c) mass in g; d) current and a; e) magnetic susceptibility in gauss-erg. f) K40KhNM; g) K40Kh20.

As can be seen from Table 5 if the length of boration is increased, and consequently the depth of the layer, the magnetic susceptibility of the alloys greatly increases. Apparently the boride layers which are formed have a magnetic susceptibility which is greater than the susceptibility of a metallic base.

Boration greatly increases the durability of cobalt and the alloys (Table 6). After boration at a temperature of 1,000°C for 6 hours, the durability of cobalt increased by 48 times, the alloy K40KhNM by 70 times and the alloy K40Kh20 by more than 100 times. Thus the durability of borated alloys and borated cobalt considerably exceeds the durability of hardened steel U12(HRC64).

Table 6

Durability of samples borated at a temperature of 1,000°C (test on the machine Shkoda-Savina. Loading 5kG, penetration depth of the disc 0.02mm).

(a) Материал образцов	(b) Длительность борирования в ч	(c) Глубина слоя (общая) в мм	(d) Износостойкость (среднее число оборотов диска)	(a) Материал образцов	(b) Длительность борирования в ч	(c) Глубина слоя (общая) в мм	(d) Износостойкость (среднее число оборотов диска)
(e) Кобальт	(f) Не борирован	—	843	К40ХНМ (i)	(f) Не борированная	—	252
	1	0,112	19 818		1	0,032	6 237
	3	0,176	31 887		3	0,064	14 904
	6	0,25	40 563		6	0,072	17 860
(h) К40Х20	(f) Не борированная	—	144	(j) У12	(g) Не борированная, закаленная (*HRC* 64)	—	13 660
	1	0,048	8 316				
	3	0,072	22 545				
	6	0,080	23 592				

a) sample materials; b) length of boration in hours; c) depth of the layer (over-all) in mm; d) duration (mean number of disc rotations)
e) cobalt; f) non-borated; g) non-borated, hardened ; h) K40Kh20; i) K40KhNM; j) U12.

A study of the effect of boration on the corrosional stability was carried out under the conditions of a tropical climate. The test lasted for 144 hours and consisted of six cycles each of which was carried out according to the following schedule: 8 hours at plus 60°C and humidity of 95%; 8 hours at plus 60°C and humidity of 100%, and 8 hours at plus 20°C and humidity of 100%. The results of the study showed that boration greatly decreases the corrosional stability. However it is" significantly greater than for steel U12 which is non-borated.

Sample material	Mean loss in weight, in n/m²	g/m²
Steel U 12, hardened, non-borated	0.00386	0.393
Non-borated cobalt	0.00085	0.087
Borated cobalt	0.00192	0.199
Non-borated K40KhNM	0.00061	0.062
Borated K40KhNM	0.00168	0.172
Non-borated K40Kh20	0.00048	0.049*
Borated K40Kh20	0.00154	0.157

* The loss in weight falls within the limit of experimental errors.

CONCLUSIONS

1. Boration of cobalt in the electrolysis of melted drill takes place more rapidly than in a melted drill with powdered carbide (30-40% weight).

2. Two zones of borides - Co_2B and CoB, which have a microhardness corresponding to H_{100} 1800 and H_{100} 1550, are formed on the surface of the borated cobalt. The general depth of both zones of boride - for instance, for a period of 3 hrs and at a temperature of 1,000°C - is 0.24mm. The surface hardness of such a layer according to Vickers (Loading 5kG) is about 950 units.

3. The alloys K40KhNM, K40Kh20 and 36NKhYuT are borated much more slowly than is cobalt. Over a period of 3 hrs and at a temperature of 1,000°C the depth of the boride zones is 0.03mm in the alloy K40KhNM and in the alloy K40Kh20 - 0.05mm. The microhardness of the borated layer of these alloys is about H_{100} 2300, i.e., greater than the microhardness of cobalt borides.

4. The durability of borated alloys and of cobalt greatly exceeds the durability of hardened, non-borated steel U12.

5. The corrosional stability of borated alloys under the conditions of a tropical climate is much lower than that of non-borated alloys but at the same time it is greater than for non-borated Steel U12.

6. Boration greatly increases the magnetic susceptibility of the alloys K40KhNM and K40Kh20.

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